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Preservation of atomically clean silicon surfaces in air by contact bonding

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When two hydrogen-passivated silicon surfaces are placed in contact under cleanroom conditions, a weak bond is formed. Cleaving this bond under ultrahigh vacuum (UHV) conditions, and observing the surfaces with low energy electron diffraction and scanning tunneling microscopy, we find that the ordered atomic structure of the surfaces is protected from oxidation, even after the bonded samples have been in air for weeks. Further, we show that silicon surfaces that have been cleaned and hydrogen-passivated in UHV can be contacted in UHV in a similarly hermetic fashion, protecting the surface reconstruction from oxidation in air. Contact bonding opens the way to novel applications of reconstructed semiconductor surfaces, by preserving their atomic structure intact outside of a UHV chamber. © 1997 American Institute of Physics.

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Clean semiconductor surfaces oxidize extremely rapidly in air. To delay this oxidation, silicon wafers can be dipped in dilute hydrofluoric acid, which strips the native oxide and results in an atomic layer of hydrogen passivating the surface.¹ Oxidation on such surfaces occurs over a period of hours.² Other approaches to passivating a clean silicon surfaces exist, such as a monolayer coverage of C₆₀,³ but again, this protects the surface from oxidation for only a few hours. We report here a simple method for long-term protection of the ordered atomic structure of a semiconductor surface in the ambient.

Contact bonding of wafers is commonly performed prior to fusion bonding at high temperatures.⁴ Simply placing two polished silicon surfaces in contact will not normally lead to adhesion, due to intervening dust particles. But under sufficiently clean conditions, contact bonding of large silicon wafers with no dust-induced voids can be achieved routinely.⁵ The adhesive forces responsible for the contact bond are believed to be weak, van der Waals type bonds,⁶ possibly mediated by surface impurities.⁷

To demonstrate that contact bonding can preserve the atomic-scale structure of surfaces under ambient conditions, we performed the following experiment in a clean room. Standard chemical-mechanically polished Si(111) wafers were coated with resist to protect the surface from particles before dicing the wafers into small chips. After removing the resist in acetone, the chips were cleaned in a 4:1 mixture of sulfuric acid and hydrogen peroxide. Then the chips were passivated in buffered hydrofluoric acid (HF:NH₄F 1:7) for 60 s, a treatment which is known to result in a flat and well-ordered Si(111) surface.⁸ After extraction from the etch bath and blow drying with nitrogen, pairs of chips were immediately contact bonded by pressing them together with tweezers, to initiate a contact wave between the surfaces.⁵ The bonded chips were left in air for some days outside the cleanroom. One of the chips was 6×6 mm², the other 10×4 mm², and they were contacted to leave two free strips on the square chip, so that it could be mounted on a

sample holder. The chips, still contact bonded, were baked at 150 °C in the load-lock of an ultrahigh vacuum (UHV) chamber for about 6 h, then transferred to the main UHV chamber, where the base pressure was 1×10^{-10} Torr. There, the two chips were gently cleaved apart with a wobble stick, leaving the square chip on the sample holder for subsequent analysis. The cleavage requires only a very slight shear force: contact bonded chips sometimes separate spontaneously under their own weight.

The resulting debonded area on the 6×6 mm² chip was observed by low energy electron diffraction (LEED) and scanning tunneling microscopy (STM). In Fig. 1(a), the Si(111)1×1 diffraction pattern characteristic of a hydrogen-terminated surface is shown, measured on the debonded area.⁹ The diffuse background, which reflects disorder on the surface, is very low and comparable to that of the clean Si(111)7×7 surface prepared in UHV.

The quality of the surface as measured by LEED is striking, considering that this particular sample had been left under ambient conditions outside the cleanroom for 15 days prior to observation.¹⁰ In previous studies, similar high-quality LEED diffraction patterns have been obtained only by extremely rapid transfer of the passivated surface to UHV, within less than 5 min of passivation, and without baking the sample in the load-lock. These precautions are necessary because slow oxidation begins immediately after extraction from the etchant.²

To illustrate this point, we show the diffraction patterns obtained under identical LEED conditions in Fig. 1(a), but after the debonded surface was placed in a load-lock which was vented to atmosphere for 2 min. The pumpdown time in the load lock was 5 min, prior to reintroduction into the main UHV chamber, without baking. The much higher diffuse background and weaker diffraction spots in Fig. 1(b) confirm the immediate damage due to brief exposure to the ambient. For samples that were cleaved in the load-lock immediately prior to pumpdown, but which were baked at 150 °C in the load-lock for several hours, the diffraction spots were barely visible. Five samples were investigated directly after debonding, and the quality of the LEED pattern was uniform over the bonded area, any decay region at the edges being less than the resolution of the LEED beam, about 0.3 mm.

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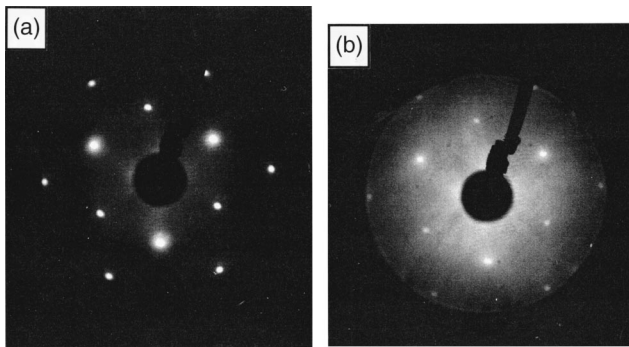


FIG. 1. (a) LEED pattern of the chemically passivated H/Si(111)1×1 surface preserved for 2 weeks under ambient conditions by contact bonding, and debonded in UHV. Electron energy is 80 eV. (b) surface preserved in identical manner to (a), but exposed to ambient conditions in load-lock for 2 min, then reintroduced into UHV. Identical LEED imaging conditions.

The atomic-scale structure of Si(111)1×1 samples debonded in UHV was observed by STM. The surface showed a terraced morphology consisting of triangular domains with typical sizes of 10–100 nm, as seen in Fig. 2. The terrace height, measured for several different images, was $2.9 \pm 0.4 \text{ \AA}$, in agreement with the monatomic step height on Si(111) of 3.1 \AA . Typically, 3–4 distinct levels of terraces are visible over $400 \times 400 \text{ \AA}^2$, giving an rms roughness of about 3 \AA on this lateral scale. Atomic resolution of the 1×1 structure of H/Si(111) could be observed on the terraces. Neither by LEED nor by STM was there evidence of the 2×1 structure that occurs when H is removed from the surface.¹¹ We conclude that the surface remains hydrogen-passivated after cleaving.

In a previous STM study of an exposed hydrogen-passivated surface transferred rapidly to UHV via a load-lock, contamination in the form of “fuzzy white balls” was observed with a density of about $1/\text{nm}^2$, and ascribed to contaminants picked up during the sample loading procedure.¹¹ We observe similar bright protrusions, but with a much lower density of less than $0.01/\text{nm}^2$. We do observe, however, that changes of the STM tip during scanning occur with a significantly higher frequency on these surfaces than on silicon surfaces cleaned by high-temperature treatment in UHV. This suggests that residual surface contaminants, not bound stably enough to be imaged, are affecting the tip. Even under cleanroom conditions, adsorption of organic contaminants during a period of less than 1 min after etching and prior to bonding is inevitable, and residual contaminants in the etchant may also adsorb. By coarse motion of the sample, we confirmed that the appearance of the surface was identical at several points over the bonded region.

To investigate contact bonding for the protection of silicon surfaces prepared under UHV conditions, we used an experimental setup that has been developed for fusion bonding in UHV.¹² Si(100) samples $2 \times 1 \text{ cm}^2$ were contact bonded in a cross formation and mounted on spring supports on a linear manipulator in a UHV chamber that was subsequently pumped down and baked. When a base pressure of 1×10^{-10} Torr was attained, the samples were separated. Caution was taken to avoid any deformation of the samples that might prevent contact bonding. Therefore, the samples were heated indirectly, by silicon strips placed underneath

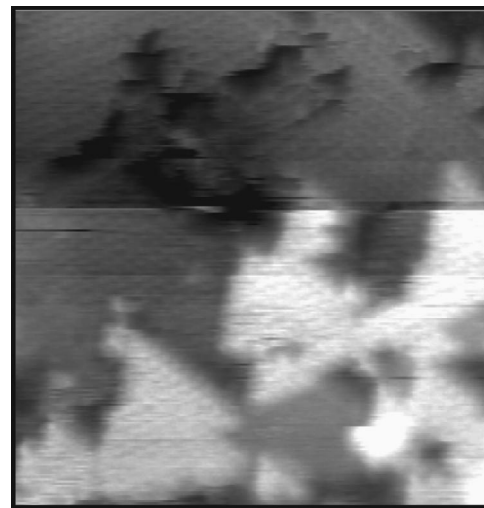


FIG. 2. $150 \times 150 \text{ \AA}^2$ area of the debonded surface imaged by STM in UHV, showing pronounced terrace structure of the chemically passivated surface. The tip is W and scanning condition is sample bias -2 V , tunnel current 0.1 nA .

them, the strips being coated with a thin nitride layer for electrical insulation. The samples were outgassed at 600°C and flashed at 850°C for several minutes. Samples prepared in this way show the characteristic 2×1 pattern of the clean reconstructed silicon surface, although there is a high diffuse background, due to the low flashing temperature, chosen to avoid thermal warping.

The samples were passivated with atomic hydrogen by heating the substrate to about 350°C , and dosing with hydrogen at 10^{-6} Torr for 6 min. A tungsten filament at 1500°C placed near the sample was a source of atomic hydrogen. This passivation procedure results in a monohydride H/Si(100)2×1 surface.¹³ After passivation, the samples were pressed gently together again. The UHV chamber was vented to air and left for 1 h under nitrogen flow. The chamber was then pumped down and baked for 12 h at 10^{-6} Torr. At a base pressure of 1×10^{-10} Torr, the samples were separated, and one of them was observed with LEED. The 2×1 pattern was still visible, with no observable deterioration [Fig. 3]. To confirm that contacting the surfaces had protected the atomic structure under atmospheric pressure, the identical venting procedure was repeated, but with the samples separated. No LEED diffraction spots were visible at all once UHV had been reestablished. We were unable to measure the strength of the bond formed when the samples are contacted in UHV, but the LEED results show that the surfaces were hermetically sealed.

Given the difficulties normally associated with maintaining UHV conditions, it may seem surprising that simply contacting two surfaces could protect them so effectively. In particular, the inherent roughness of the surfaces does not appear to lead to any significant trapping or leaking of gas in the bonded region. Given the terrace structure of the Si(111) surface in Fig. 2(a), there must be a labyrinth of nanochannels between the wafers when two such surfaces are contact bonded, although the elastic distortions due to attraction between the surfaces will tend to narrow these channels.¹⁴ A conservative estimate of the capacity of this labyrinth, ignoring elastic effects, can be obtained by assuming an average

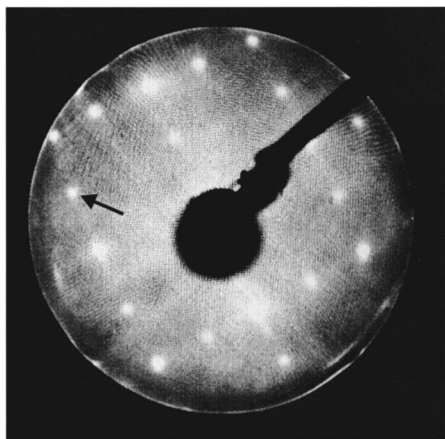


FIG. 3. LEED pattern of H/Si(100) 2×1 reconstructed surface after contacting in UHV and venting chamber 1 h. After restoration of UHV, the surfaces are moved apart and one is imaged. Half-order peak due to the 2×1 surface reconstruction indicated by arrow. The high background is intrinsic, due to the surface preparation procedure prior to venting the chamber.

separation between the wafers of about twice the measured roughness (about 2 atomic layers). This corresponds to about 0.002 ML coverage of oxygen, compatible with the low defect density observed by STM. Leakage of air via the nanochannels into the bonded regions, if it occurs at all, is apparently insignificant on the time-scale of these experiments. Leaks may be sealed by elastic distortions of the surfaces, or by oxidation around the edge of the bonded area.

Whatever the detailed mechanism, our results show that contact bonding is in practice an extremely effective protection of the atomic structure of a surface from the environment. We see several potential applications for this technique. As demonstrated here, it provides a contamination-free way to transfer chemically prepared silicon surfaces into UHV for study by standard surface analytical tools. It is common to chemically passivate silicon surfaces prior to introduction into UHV chambers for thin film growth techniques such as chemical vapour deposition;¹⁵ contact bonding followed by debonding in UHV could greatly reduce contamination of the surfaces prior to growth. Contact bonded silicon wafers could be transferred between separate UHV processing chambers without requiring a UHV transport chamber. Contact bonding can be achieved on other semiconductors such as GaAs¹⁶ and insulators such as quartz,¹⁷ provided they are thin and flat enough. Although hydrogen-passivated silicon surfaces have been used here, contact bonding can be achieved with a wide variety of sur-

face terminations such as hydrophilic groups^{6,7} and absorbed layers such as C₆₀.¹⁸

Being able to preserve UHV-prepared surfaces under ambient conditions also has interesting perspectives. The “micro-UHV” conditions that bonding provides could be exploited in devices based on the unique electronic properties displayed by the clean and adsorbate-induced reconstructions of semiconductor surfaces in UHV. Until now, no method has existed to maintain these properties outside of UHV. Thus, contact bonding of semiconductor surfaces in UHV may allow practical access to the properties of atomically clean surfaces, which have been studied for over 30 years in inconveniently large vacuum chambers.

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⁹Analogous experiments have been carried out for Si(100) samples etched in dilute HF (10%) prior to contact bonding, and a 1×1 diffraction pattern of comparable quality was obtained.

¹⁰By Auger electron spectroscopy, we were not able to detect oxygen or fluorine on the samples, implying less than 2% coverage of these contaminants. A significant carbon signal was detected, consistent with other studies of HF-passivated surfaces.

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